

# Compositional and structural changes in $ZrO_xN_y$ films depending on growth condition

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## Abstract

The present work focuses on the analysis of  $ZrO_xN_y$  thin films, the composition evolution with changing growth conditions and its relation with the structural and morphological properties of the films. The films were prepared by rf reactive magnetron sputtering, using different reactive gas flows. Composition and structure were measured combining ion beam analysis (IBA) and X-ray diffraction (XRD) techniques. The depth profiles of nitrogen and oxygen have been obtained by elastic recoil detection analysis (ERDA).

Results showed that the oxygen fraction in the films increases with gas flow, reaching a value of  $x \sim 0.33$  for a reactive gas flow mixture of 6.25 sccm. During growth mixed zirconium nitride and oxide phases form. Furthermore, the deposition rate correlates with the oxygen content variations, showing a continuous decrease with reactive gas flow.

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## 1. Introduction

The fourth-group transition metal mononitrides,  $MeN$  ( $Me = Ti, Zr, Cr, V$ , etc.), have been of extensive commercial interest for many years due to their optical and mechanical properties. The unique combination of metallic and covalent bonding characteristics [1,2] lead to properties such as high melting point, hardness, wear resistance, brittleness as well as good thermal and chemical stability and corrosion resistance [1–3]. Metallic properties such as electrical conductivity and metallic reflectance, together with

the aesthetic property of their prominent colorations in the visible wavelength region [4] make their applications as coatings for decorative objects advantageous.

Recently, the influence of the microstructure, e.g., created by the ion bombardment during rf sputtering growth, on the material coloration was investigated [4,5]. This correlation between microstructure and coloration has been shown to be important, and especially when new elements are introduced to the base nitride. A major role is played by oxygen which allows the tailoring of film properties between those of metallic nitrides and the correspondent largely ionic oxides [6–8].

The aim of this work has been to study the influence of deposition conditions such as the reactive gas mixture flow and ion bombardment on some of the properties of magnetron sputtered  $ZrO_xN_y$  thin films.

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## 2. Experimental details

The  $ZrO_xN_y$  samples were deposited by reactive rf magnetron sputtering onto single crystalline (100) silicon using a high purity Zr target. Prior to growth the substrates were ultrasonically cleaned and sputter-etched for 15 min in a 0.4 Pa Ar atmosphere (200 W rf power). Depositions were carried out in an Ar/N<sub>2</sub> + O<sub>2</sub> atmosphere in an Alcatel SCM650 apparatus. The substrates were rotating 60 mm above the target at a constant speed of four rotations per minute. The base pressure in the deposition chamber was about 10<sup>-4</sup> Pa and rose to values around 4 × 10<sup>-1</sup> Pa during growth. Substrates were heated up to  $T_s = 300$  °C and dc biased with values between -50 V and ground. Films were prepared with variation of the gas mixture (N<sub>2</sub> + O<sub>2</sub>) flux, using constant values of temperature (300 °C). Reactive gas flows varied from 3.75 to 6.25 sccm, with a partial pressure ranging from 0.02 to 0.05 Pa. Argon flow was kept constant at 100 sccm.

The chemical composition of the as-deposited films have been determined by Rutherford backscattering spectrometry (RBS), using 1.4 and 2.0 MeV proton and <sup>4</sup>He<sup>+</sup> beams, respectively, and Elastic Recoil Detection Analysis (ERDA) using a 40 MeV Cl<sup>7+</sup> beam. The ERDA spectra were collected at 30.76° for an incidence angle of  $\theta = 75^\circ$ . A Bragg ionisation chamber was used to detect the scattered Cl ions and the recoils. Two signals were extracted, one proportional to the energy of the detected species, the other proportional to their atomic number, leading to 2D spectra. The data were analysed with the IBA DataFurnace NDF v7.9a [9]. All spectra of a given sample were analysed simultaneously in a self-consistent manner, to ensure all information is properly taken into account to obtain the final result. ZBL 2000 stopping powers were used. X-ray diffraction (XRD) experiments were performed using a Philips PW 1710 apparatus (Cu K<sub>α</sub> radiation).

## 3. Results and discussion

Using the NDF code the simulation of the experimental RBS data revealed that, although oxygen is extremely reactive in comparison with nitrogen [10], a large range of O contents is deposited. ERDA showed that compositional homogeneity with depth is obtained in all coatings, with no significant fluctuations of the chemical composition through the analyzed (~200 nm) thickness of the films. This is illustrated in Fig. 1. In all the films studied a small oxygen surface peak was found. The oxygen and nitrogen content fractions (normalized to the zirconium content) will be quoted in the text as subscripts x and y, respectively. The oxygen fraction has been determined from the ratio of the oxygen content and the sum of both oxygen and nitrogen content:  $f_{O_2} = C_O / (C_O + C_N)$ . The variation of the deposition rate with both oxygen fraction and bias voltage applied to the substrates is plotted in Fig. 2. The results plotted in this graph show a tendency for a decrease in the deposition rate with the increase of the oxygen fraction,

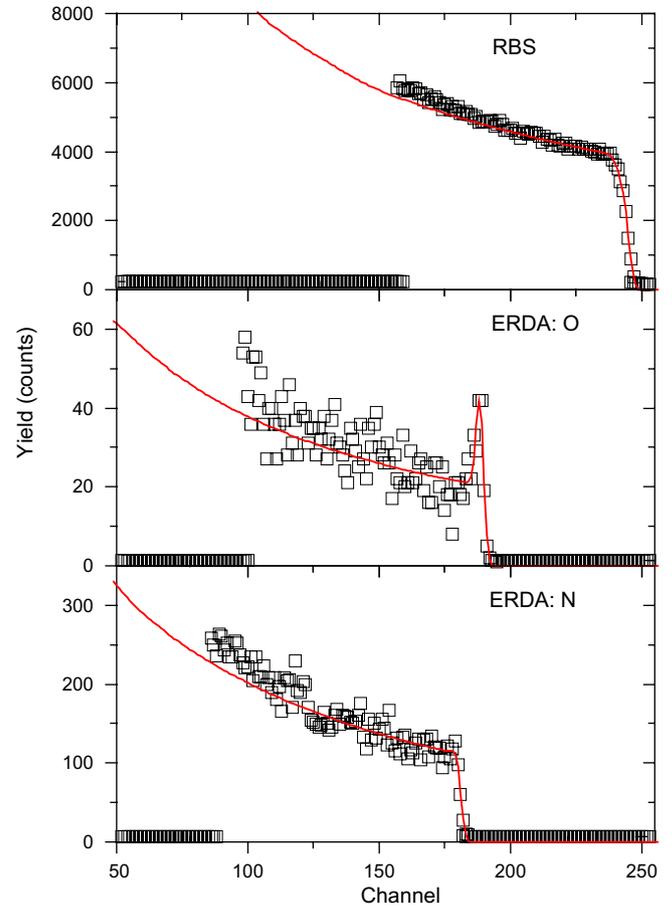


Fig. 1. RBS and ERDA spectra of a  $ZrO_{0.28}N_{0.85}$  film. A constant composition was observed through the entire probing depth (~200 nm) below the surface region, where a small oxygen peak is evident.

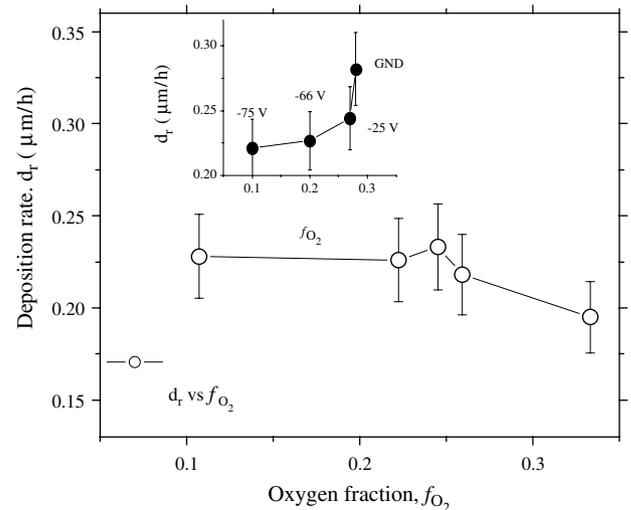


Fig. 2. Measured deposition rate,  $d_r$ , versus the oxygen incorporated in the films at -50 V. Insert shows the dependence on the bias voltage applied to the substrates.

which is particularly evident at the highest flows. This decrease in the deposition rate can be explained taking into account the occurrence of the so-called target poisoning by

both oxygen and nitrogen reactive gases [10]. Particularly noticeable is the result revealed by the unbiased sample, which shows a relatively higher deposition rate in comparison to those prepared with biased substrates. The decrease in the deposition rate for negatively biased experiments is a consequence of the increase in the bias current,  $I_s$ , promoted by the ion bombardment of the growing films. This ion bombardment causes not only a densification of the growing film, but also some re-sputtering of deposited species, decreasing the deposition rate [10]. In this sense, it is worth noticing that the oxygen fraction in the negatively biased samples changes from 0.28 to 0.10, as it can be seen in the upper insert of Fig. 2. From these results, it is clear that the bias voltage (correlated with ion bombardment conditions during growth) is a very important factor for the growth rate, since the grounded sample has an oxygen fraction of  $\sim 0.28$ , but its deposition rate is significantly higher than that corresponding to the sample prepared at  $-50$  V (plot versus  $f_{O_2}$ ).

The growth changes mentioned above can also be seen in Fig. 3, showing the X-ray diffraction patterns of the different samples. For the lower gas flows (lower oxygen contents), the films crystallize in a B1-NaCl crystal structure, typical for ZrN. Furthermore, with increasing oxygen fraction, the (200) peak intensity shows a tendency to decrease. In particular for the sample with an oxygen fraction of 0.33 the (111) peak intensity is even higher than that of the (200) one, hence foreseeing a preferential crystalline growth change. The effect of the increasing reactive gas and mainly the amount of oxygen (and the correspondent variation in deposition rate, Fig. 2) is a parameter to take into account for this variation. In fact, a closer look at the results for the sample grown with an oxygen fraction of 0.33 reveals that a second crystalline phase might be already present. The diffraction peak located at  $2\theta = 32.6^\circ$  presents a shift from the (111) reference ZrN

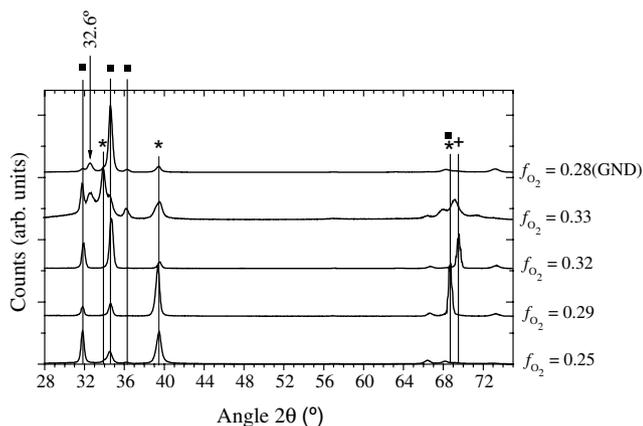


Fig. 3. X-ray diffraction spectra for films with increasing oxygen content. In the figure the asterisk,  $\star$  correspond to fcc ZrN phase (respectively (111), (200) and (311) planes with increasing angular positions); solid squares,  $\blacksquare$ , to the reflections of Zr from the adhesion layer and the cross,  $\times$ , to the silicon from the substrate.

of about  $2^\circ$ . One possibility is that this could be the result of the formation of an oxygen doped zirconium nitride phase, resulting in a structure close to that of  $Zr_3N_4$  [11]. Some authors have already reported the shift of the (111) peak of the ZrN (NaCl type phase) towards smaller angles for films prepared with high nitrogen flows [12], resulting in the development of that poorly crystallized  $Zr_3N_4$  phase. This phase is known to be formed as a result of cell expansion by incorporation of nitrogen (and oxygen) atoms in interstitial positions [11,12] or as a relaxed NaCl structure with some Zr vacancies [12]. Anyway, in the case presented here, the reduced number of diffraction peaks does not allow further conclusions about the exact nature of the crystalline phase that is formed. The sample prepared without ion bombardment,  $ZrO_{0.32}N_{0.81}$ , also presents the same phase. Nevertheless, this sample presents a composition very similar to a sample prepared with ion bombardment,  $ZrO_{0.28}N_{0.85}$ , which shows in its turn no traces of this phase. The absence of ion bombardment and thus the reduced surface mobility means that adatoms do not have enough superficial energy to form different phases or segregate mixed phases, and thus the increasing tendency to form doped phases. Furthermore, the sample prepared with no ion bombardment presents a total amount of nitrogen + oxygen,  $x + y$ , of about 1.3, which is lower than that of 1.5 in the sample with 0.33 oxygen fraction, showing that the presence of oxygen is fundamental, but also the surface mobility conditions.

#### 4. Conclusions

Combining RBS and ERDA analysis the compositional depth profile of  $ZrO_xN_y$  films was determined. The increase of O content correlates with the deposition rate. It was also found that oxygen has a strong influence on the growth process of the films possibly interfering with the mobility of the adatom species. X-ray revealed the presence of different phases depending on the amount of oxygen in the film.

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